Investigating a New Approach for Harvesting Low-grade Thermal Energy Using an Electrochemical System

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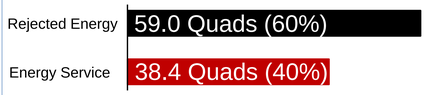
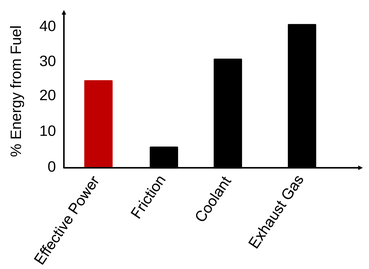
Motivation

2013 US Energy Use [1]



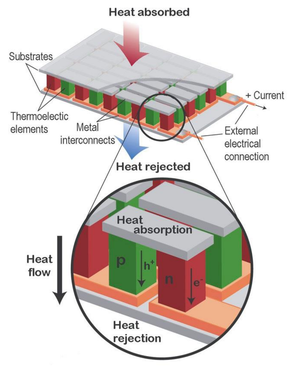
1 Quad = 1.055 × 10^{18} Joules

Internal Combustion Engine [2]



Classical solid-state thermoelectric generators potentially provide an approach to improve the efficiency of those systems by **converting waste heat directly into useful electricity**, but have limited applications due to their **low energy conversion efficiency** and **low-abundance elements** that pose challenges for scale-up, as they entail **high material costs**.

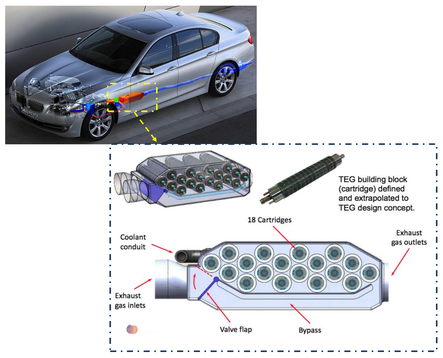
How Does It work?



N-type semiconductors:
More electrons than holes (empty states)

P-type semiconductors:
More holes than electrons

An Example Of Its Application [3]



ZT - Efficiency Definition

$$ZT = \frac{\sigma S^2 T}{\lambda}$$

Research Approach

Research Objectives

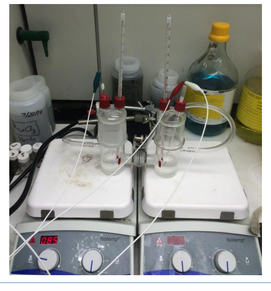
Theoretical Study:

- To investigate the thermopower of electrolytes as a function of temperature gradients and proton concentration gradients.
- To find an alternation to classical solid-state thermoelectric materials

Experimental Study:

- To test the thermopower of electrolytes and experimentally prove our principle.

Experiment Set-up



Experiment Conditions

Substance used in this research:

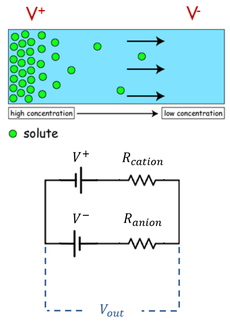
120 ml 15M Nitric Acid (HNO_3) and 20 grams $Ba(NO_3)_2$

Operating Temperature:

293 K ~ 343 K (20 ℃ ~ 70 ℃)

Theoretical Study

Thermopower & Conductivities of Bipolar Ions Transport



Ions Movements Resistance, R, depends on: [5]

Molar concentrations of ions, v_c,
Faraday's constant ($F = N_A e$),
Ions' mobility, u,
Ions' charge, z,
Length of the channel, l:

$$R = \frac{l}{zuv_cFA}$$

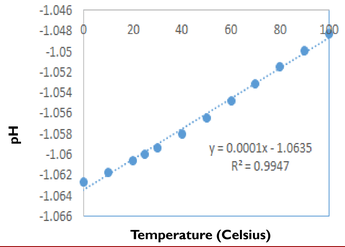
Output voltage then depends on:

$$V = \frac{V_+\beta + V_-}{\beta + 1} \qquad \beta = \frac{u_+}{u_-}$$

This is the key to the new device. In the presence of a concentration gradient (internal voltages), if an electrolyte in which cations have larger ions mobility and charges than anion, then the system should generate electricity.

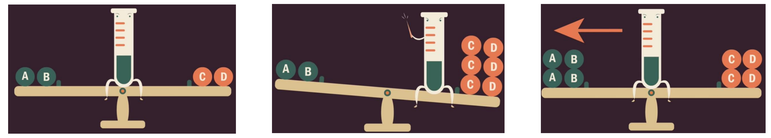
Ions' Mobility

Ions	Mobility
H^+	36.30 × 10^{-4}
NO_3^-	7.40 × 10^{-4}
Ba^{++}	6.59 × 10^{-4}



Concentration Gradient

Le Chatelier's Principle:



Reversible Reaction:

$$Ba(NO_3)_2 \overset{K_{sp}}{\Leftrightarrow} Ba^{2+} + 2NO_3^-$$
$$HNO_3 \overset{K_a}{\Leftrightarrow} H^+ + NO_3^-$$
$$Ba(NO_3)_2 + HNO_3 \Leftrightarrow Ba^{2+} + H^+ + 3NO_3^-$$

Proton (H+) Concentration:

$$[H^+] = \sqrt{\frac{[Ba^{2+}][K_a]^2}{K_{sp}}}$$

as a function of temperature

Thermopower of Proton as an Ideal Gas

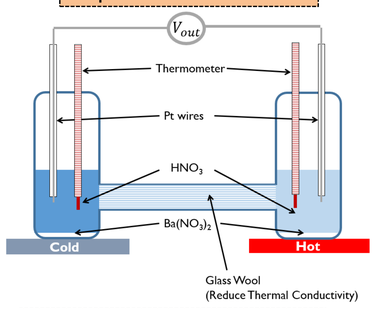
Concentration Gradient → Electrochemical Gradient → Electric Field

$$\alpha \equiv \frac{V}{\Delta T_x} = \frac{C_v}{ne} = \frac{k_B}{e}\left(1 + \frac{d\ln(n)}{d\ln(T)}\right) = 593\ \mu V/K$$

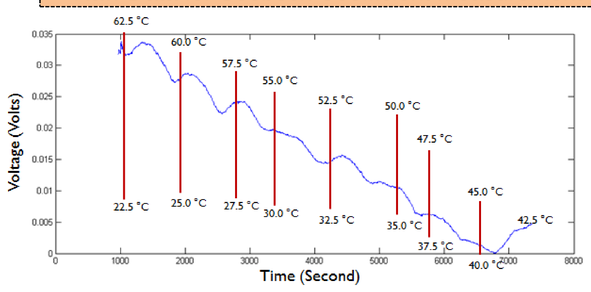
C_v: Specific heat per constant volume of the whole system.
α : Thermopower of an ideal gas is the entropy per particle.
ξ : Electric field at position x
n : Proton concentration

Experimental Study

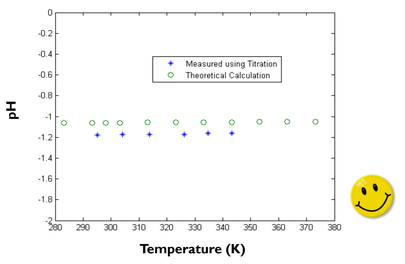
Experiment Schematic



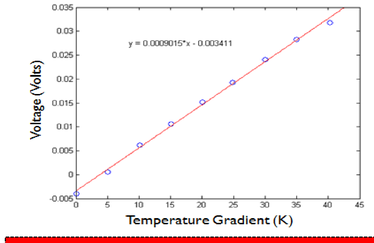
Raw Data for Seebeck Coefficient Measurement



pH Measurement

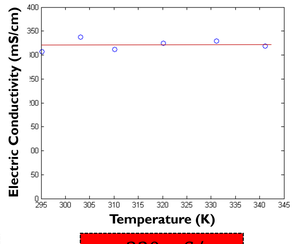


Seebeck-like Coefficient: S



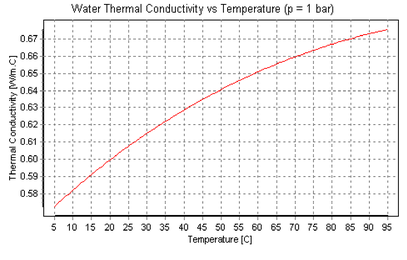
$\alpha = 901.5\ \mu V/K$: Compare Well with Our Theory

Electric Conductivity: σ

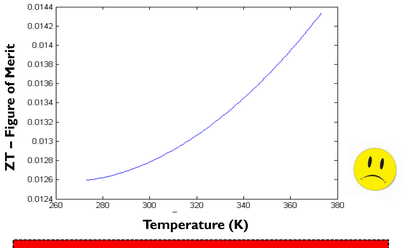


$\sigma = 320\ mS/cm$

Thermal Conductivity (Water): λ [4]



ZT – Figure of Merit



$ZT \approx 0.0134$: Changes with Temperature

Conclusion

- The experimental study reproduce the theoretical value quiet well, without the use of any adjustable parameters which means our principle works!
- Nitric acid and barium nitrate system would be able to reach an energy conversion of 1% by just changing the geometry of the reaction cell – short channel for reducing resistivity.
- This principle provide a potential approach for harvesting low-grade waste heat.

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Reference

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